

REMARKS

In paragraph three of the Office Action, claims 27-39 and 41-60 were rejected under 35 U.S.C. §103(a) as being unpatentable over Sakon et al. (U.S. Patent No. 5,560,857) in view of Stanford et al. (U.S. Patent No. 5,244,000) and Kern (Hand Book of Semiconductor wafer cleaning technology) and further in view of Sehested et al. (J.Phys.Chem.).

In one aspect, the current invention discloses a process wherein ozone in combination with a scavenger removes organic contamination on a substrate. Applicants do not believe that the references alone, or taken in combination, render the claims obvious for at least three reasons.

First, the invention is directed to the removal of organic contaminants resulting from a previous lithographic step rather than directed to the removal of metallic contaminants (which is the subject of the Sakon reference). As discussed in paragraph 4 of the enclosed Declaration of Stefan DeGendt, one of the inventors of the present application, there is a substantial difference between the removal of organic contaminants (and especially the removal of organic contaminants resulting from a previous lithographic step) and the removal of metallic contaminants.

As discussed in paragraph 5 of the enclosed declaration, a typical wet cleaning sequence is SC1 step and then SC2 step. The SC1 step is typically an alkaline oxidizing step, used to remove particles in general, but is prone to introducing metallic contamination, requiring a further process step (e.g., SC2 step). The SC2 step is typically an acid oxidizing step, used to remove metallic species. The cleaning from the SC1 and SC2 steps is surface (monolayer)

cleaning. This cleaning sequence is generally known as an RCA clean and has been introduced by Werner Kern 'RCA Rev. 31, 1970, p.187.

When thicker (visible) layers or residues must be removed, such as a layer of organic photoresist, at least extra processing steps are added. Typically, the sequence is as follows: SPM (sulphuric peroxide mixture) step, then diluted HF step, then SC1 step, and then SC2 step. SPM is a very oxidizing substance which very aggressively removes organic contaminants (such as those caused by a previous lithographic step). The SPM step is typically followed by a step in which diluted HF is applied. After the diluted HF step, the SC1 and SC2 steps are applied to further clean the substrate. The claims currently pending give an alternative to the SPM step. As discussed in the background section of the patent, the SPM step has several disadvantages including: (1) using expensive chemicals; (2) requiring high processing temperatures; and (3) causing serious problems in terms of chemical waste treatment of the sulphuric peroxide mixture. Thus, the present invention avoids the need for using, for example, the caustic substance of the sulphuric peroxide mixture. Instead, a much more environmentally friendly liquid comprised of water, ozone and an additive acting as a scavenger is used, as claimed in claims 27, 51 and 60. See paragraph 8 of Declaration of Stefan DeGendt.

The prior art actually teaches away from the use an SC2 step in a photoresist removal step. For example, the appended article by Werner Kern entitled "The Evolution of Silicon Wafer Cleaning Technology," *J. Electrochem. Soc.*, Vol. 137, June 1990, discusses SC1 and SC2 steps. In the second full paragraph on page 1888, Mr. Kern describes an SC1 step, as shown in the following excerpt:

In the first treatment step, the wafers are exposed to a hot mixture of water-diluted hydrogen peroxide and ammonium hydroxide. This procedure was designed to remove organic surface films by oxidative breakdown and dissolution to expose the silicon or oxide surface for concurrent or subsequent decontamination reactions.

Mr. Kern, again on page 1888, third full paragraph, describes an SC2 step, as shown in the following excerpt:

The second treatment step exposes the rinsed wafer to a hot mixture of water-diluted hydrogen peroxide and hydrochloric acid. This procedure was designed to remove alkali ions and cations such as Al^{+3} , Fe^{+3} , and Mg^{+2} , that form NH_4OH -insoluble hydroxides in basic solutions.

On page 1888, in the paragraph beginning with "optional processing steps," a preliminary clean-up treatment with a hot SPM is mentioned, as discussed in the following excerpt:

A preliminary clean-up treatment with a hot $H_2SO_4-H_2O_2$ mixture (2:1 vol) can be used advantageously for grossly contaminated wafers having visible residues, such as photoresist layers.

Mr. Kern concludes that the chemistry of an SC2 step is not for photoresist removal, as discussed on page 1888 (bottom left paragraph):

However, using high-purity and point-of-use ultrafiltered and particle-free HF solution is used under controlled conditions, more harm than good can result. A silicon surface that was exposed to HF is highly reactive and immediately attracts particles and organic contaminants from solution, DI water, and ambient air. Contrary to SC-1, the subsequent SC-2 solution, which has no surfactant activity, will not eliminate these contaminants.

(Emphasis added). Stefan DeGendt, in his declaration, concludes that not every mixture of an inorganic acid (e.g. HCl) and hydrogen peroxide are capable of removing organic contaminants from silicon substrates. See paragraph 7 of Declaration of Stefan DeGendt. Thus, the Kern reference on page 1888 clearly states that the SC2 step will not affect the removal of photoresist.

Second, the invention calls for the use of ozone rather than the use of hydrogen peroxide (as taught in the Sakon reference). Contrary to the assertion by the Examiner, ozone is not interchangeable with hydrogen peroxide, as discussed in the appended declaration. As an initial matter, ozone is much more environmentally friendly than hydrogen peroxide. See paragraph 9 of Declaration of Stefan DeGendt. Moreover, the reactivity of ozone is much higher than hydrogen peroxide. Specifically, in order to provide the necessary reactivity in a hydrogen peroxide mixture, the concentration of the hydrogen peroxide is typically greater than 10% whereas for the equivalent reactivity in an ozone mixture, the concentration of ozone is in the parts per million (ppm) range. *Id.* Finally, ozone is much cheaper to use than hydrogen peroxide. As discussed previously, the concentration of hydrogen peroxide must be above a certain percentage in order to achieve the desired reactivity. Over time, use of the bath decreases the concentration of the hydrogen peroxide, requiring the replacement of the bath or the addition of hydrogen peroxide. By contrast, ozone need only be bubbled up in the mixture, making processing significantly easier. *Id.*

Third, Sakon discloses the use of acetic acid but for an entirely different purpose – not for use as a scavenger, as recited in each of the claims. The Examiner states that the Sakon reference must only teach that the use of acetic acid provides some advantage in the cleaning composition. Applicants respectfully disagree. A general teaching regarding the benefit of using acetic acid, without more, is an insufficient teaching to those skilled in the art to use acetic acid as a scavenger. Rather, there must be some suggestion to use acetic acid as a scavenger. Clearly, the Sakon reference provides no such teaching and therefore does not render the claims obvious.

Moreover, the Stanford reference is different from the present invention for at least the reasons stated with respect to the Sakon reference.

/ In paragraph five of the Office Action, claim 49 was provisionally rejected under 35 U.S.C. §101 as claiming the same invention as claim 27 of co-pending Application Serial No. 09/207,546. Applicants have amended claim 27 in co-pending Application Serial No. 09/207,546.

/ In paragraphs seven and eight of the Office Action, claim 27, 51, and 60 were provisionally rejected under judicially created doctrine of obvious-type double patenting. Upon allowance of claims in the present cases, applicants will submit a terminal disclaimer in the co-pending case.

CONCLUSION

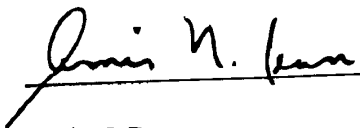
If for any reason, the application is not considered to be in condition for allowance on the next Office Action and an interview would be helpful to resolve any remaining issues, the Examiner is requested to contact the undersigned attorney at (312) 913-0001.

Respectfully submitted,

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Dated: 8/24/01

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APPENDIX UNDER 37 CFR 1.121(c)

27. (Thrice Amended) A method for removing organic contaminants from a substrate, the organic contaminants resulting from a previous lithographic step, the method comprising the steps of:

contacting at least one side of said substrate with a liquid comprising water, ozone and an additive acting as a scavenger, wherein the proportion of said additive in said liquid is less than 1% molar weight of said liquid; and

maintaining said liquid at a temperature less than the boiling point of said liquid.

51. (Twice Amended) A method for removing organic contaminants from a substrate, the organic contaminants resulting from a previous lithographic step, the method comprising the steps of:

contacting at least one side of said substrate with a liquid comprising water, ozone and an additive acting as a scavenger, wherein said liquid is comprised substantially of water; and

maintaining said liquid at a temperature less than the boiling point of said liquid.

60. (Twice Amended) A method for removing organic contaminants from a substrate, the organic contaminants resulting from a previous lithographic step, the method comprising the steps of:

holding said substrate in a tank; and

filling said tank with a fluid comprising water, ozone and an additive acting as a scavenger, and wherein the fluid is comprised substantially of water.

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The Evolution of Silicon Wafer Cleaning Technology

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ABSTRACT

The purity of wafer surfaces is an essential requisite for the successful fabrication of VLSI and ULSI silicon circuits. Wafer cleaning chemistry has remained essentially unchanged in the past 26 years and is based on hot alkaline and acidic hydrogen peroxide solutions, a process known as "BCA Standard Clean." This is still the primary method used in the industry. What has changed is its implementation with optimized equipment: from simple immersion to centrifugal spraying, megasonic techniques, and enclosed system processing that allow simultaneous removal of both contaminant films and particles. Improvements in wafer drying by use of isopropanol vapor or by "slow-pull" out of hot deionized water are being investigated. Several alternative cleaning methods are also being tested, including alkaline solutions, chemical vapor etching, and UV/ozone treatment. The evolution of silicon wafer cleaning processes and technology is traced and reviewed from the 1950s to August 1989.

The importance of clean substrate surfaces in the fabrication of semiconductor microelectronic devices has been recognized since the early days of the 1950s. As the requirements for increased device performance and reliability have become more stringent in the era of VLSI and ULSI silicon circuit technology, techniques to avoid contamination and processes to generate very clean wafer surfaces have become critically important. Besides, over 80% of yield losses in integrated circuit fabrication are generally accepted to be due to microcontamination. Trace impurities, such as sodium ions, metals, and particles, are especially detrimental if present on semiconductor surfaces during high-temperature processing (thermal oxidation, diffusion, epitaxial growth) because they may spread and diffuse into the semiconductor interior. Impurities must also be removed from surfaces before and/or after lower temperature steps, such as chemical vapor deposition, dopant implanting, and plasma reactions. Particulate after photoresist stripping is necessary for every mask level throughout the production process.

Many wafer cleaning techniques have been tested and several are being used. The generally most successful approach for silicon wafers without metallization uses wet-chemical treatments based on hydrogen peroxide chemistry. This process has remained essentially unchanged during the past 26 years, but important advances have been made in its technical implementation. The evolution of the cleaning technology for premetallized silicon wafers from its beginning to the present time will be traced in this paper.

Type, Origin, and Effects of Contaminants

Impurities on silicon wafer surfaces occur in essentially three forms: (i) contaminant films, (ii) discrete particles, and (iii) adsorbed gases that are of little practical consequence in wafer processing. Surface contaminant films and particles can be classified as molecular compounds, ionic materials, and atomic species. Molecular compounds are mostly particles or films of condensed organic vapors from lubricants, greases, photoresist, solvent residues, components from plastic storage containers, and metal oxides or hydroxides. Ionic materials comprise cations and anions, mostly from inorganic compounds that may be physically adsorbed or chemically bonded (chemisorbed), such as sodium ions, fluoride ions, and chloride ions. Atomic or elemental species comprise metals, such as gold and copper, that may be electrochemically plated out on the silicon surface from HF-containing solutions, or they may consist of silicon particles or metal debris from equipment.

The sources of impurities are manifold. In the case of particles, which can be detected and measured much more easily than contaminant films, the major sources are equipment, chemicals, factory personnel, and production processes. For example, mechanical equipment, process operators, furnace tubes, film deposition systems, gas piping,

and liquid containers are especially serious sources, whereas materials, liquid and gaseous chemicals, and ambient air tend to cause less particle contamination; but all contribute significantly to the generation of contaminant films. Static charge built up on wafers and carriers is a powerful mechanism of particle deposition, but is often overlooked and not properly dealt with.

Molecular contaminant films on wafer surfaces can mask effective cleaning or rinsing, cause poor adhesion of deposited layers, and lead to harmful decomposition products. For example, organic films, if heated to high temperatures in a nonoxidizing atmosphere, can carbonize and form silicon carbide that can nucleate polycrystalline regions in an epitaxial deposit. Ionic films and metals cause a host of problems in semiconductor devices. During high-temperature processing or on application of an electric field they may diffuse into the bulk of the semiconductor structure or spread on the surface, leading to electrical defects, device degradation, and yield losses. For example, highly mobile alkali ions may cause drift currents and unstable surface potential, shifts in threshold and flatband voltages, surface current leakage, and may lower the oxide breakdown field of thermally grown layers. In the growth of epitaxial silicon layers, sufficiently high concentrations of ions can give rise to twinning dislocations, stacking faults, and other crystal defects. Atomic metals, especially the heavy metals, can affect minority-carrier lifetime, surface conduction, electrical device stability, and lead to structural defects in epitaxial layers. Particles may cause blocking in photolithography and etching or rinsing, and lead to shorts if they are conductive and located adjacent to conductor lines. They are considered potential killer defects if their size exceeds one tenth of the linewidth. Particles that are present during film growth or deposition may lead to pinholes, material voids, cracks, and the generation of defects noted above, depending on their chemical composition. Additional information on the nature, origin, detection, and effects of contaminants is available from selected papers and reviews (1-18).

Early Cleaning Procedures

During the early stages of silicon wafer processing until about 1970, one used organic solvent extraction, boiling nitric acid, aqua regia, concentrated hydrofluoric acid, and hot acid mixtures as cleaning chemicals. Mixtures of sulfuric acid-chromic acid led to chromium contamination and caused ecological problems or disposal. Mixtures of sulfuric acid and hydrogen peroxide caused sulfur contamination. Aqueous solutions containing hydrogen peroxide had long been used for cleaning electron tube components (14, 15) but not for semiconductors. In general, impurity levels and particles in process chemicals were high and in themselves tended to lead to further contamination. Particulate impurities were removed by ultrasonic treatment in detergent solutions or by brush scrubbing. The first caused frequent wafer breakage and the second often deposited more debris from the bristles than it removed from the wafer surfaces.

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Cleaning Processes Based on Hydrogen Peroxide Solutions

Cleaning chemistry.—The first systematically developed cleaning process for bare or oxidized silicon wafers was based on a two-step oxidizing and complexing treatment with hydrogen peroxide solutions: (i) an alkaline mixture at high pH followed by (ii) an acidic mixture at low pH (1). The choice of chemicals was based on reaction chemistry, oxidation potentials, reagent purity, reagent volatility, safety, and economy. The process was developed at RCA, introduced to device production in 1988, and published in 1970 (1).

In the first treatment step the wafers are exposed to a hot mixture of water-diluted hydrogen peroxide and ammonium hydroxide. This procedure was designed to remove organic surface films by oxidative breakdown and dissolution to expose the silicon or oxide surface for concurrent or subsequent decontamination reactions. Group IB and IIB metals and several other metals, including gold, silver, copper, nickel, cadmium, zinc, cobalt, and chromium, are dissolved and removed by the complexing effectiveness of ammonium hydroxide; copper, for example, forms the $\text{Cu}(\text{NH}_3)_4^{2+}$ amino-complex.

The second treatment step exposes the rinsed wafers to a hot mixture of water-diluted hydrogen peroxide and hydrochloric acid. This procedure was designed to remove all metal ions and cations such as Al^{3+} , Fe^{3+} , and Mg^{2+} , that form NH_4OH -insoluble hydroxides in basic solutions. This second step also eliminates metallic contaminants that were not entirely removed by the first treatment, such as gold. Electrochemical displacement replating of heavy metals from the solution is prevented by formation of soluble complexes with the dissolved metal ions.

Solution composition, process conditions, and effectiveness.—The solution compositions are based on ultrafiltered deionized water, electronic grade NH_4OH (20 weight percent w/o) as NH_3 , electronic-grade HCl (37 w/o), and high-purity "unstabilized" H_2O_2 (30%). The hydrogen peroxide must be low in aluminum and stabilizer additives (sodium phosphate, sodium stannate, or amino derivatives) to prevent wafer recontamination. The usual volume ratios for the solution used in the first treatment step are 5 H_2O_2 :1 NH_4OH ; the mixture is known as "RCA standard clean 1 or SC-1." The usual volume ratios for the second solution are 6 H_2O_2 :1 H_2O :1 HCl "RCA standard clean 2, or SC-2." Treatments by the original immersion technique are typically 10 min at 75°–80°C in each solution. Higher temperatures must be avoided to minimize excessive thermal decomposition of the hydrogen peroxide. Intermediate and final rinses in ultrafiltered deionized water are used.

The effectiveness of the process was demonstrated by sensitive radioactive tracer measurements with several radionuclides (1, 18) and by capacitance-voltage bias temperature measurements of MOS capacitors (1). H_2O_2 solutions are unstable at elevated temperature, especially at high pH, rapidly decomposing to H_2O and O_2 . The processing temperature should therefore be kept at 75°–80°C to sufficiently activate the mixtures without causing excessively fast decomposition.

Optional processing steps.—A preliminary clean-up treatment with a hot H_2SO_4 - H_2O_2 mixture (3:1 vol) can be used advantageously for grossly contaminated wafers having visible residues, such as photoresist layers. Another step, not noted in the original paper (1), concerns an etch in HF solution for bare silicon wafers. Since the hydrous oxide film from the SC-1 treatment may trap trace impurities, its removal before the SC-2 step should be beneficial. A 18s immersion in 1% HF - H_2O solution is sufficient to remove this film, as evidenced by the change from the hydrophilic oxidized surface to hydrophobic after stripping. However, unless high-purity and point-of-use ultrafiltered and particle-free HF solution is used under controlled conditions, more harm than good can result. A silicon surface that was exposed to HF is highly reactive and immediately attracts particles and organic contaminants from solutions, DI water, and the ambient air. Contrary to SC-1, the

subsequent SC-2 solution, which has no surfactant activity, will not eliminate these contaminants. It may therefore be preferable to rely on the dissolution action of SC-1 that dissolves and regrows the hydrated oxide layer at about the same rate. If the pre-clean is used, then the 1% HF step prior to SC-1 is acceptable since SC-1 will remove the contaminants. Exposure of bare silicon wafers to HF after SC-2 should not be done since it would destroy the passivated surface resulting from SC-2 and cause recontamination.

Immersion technique.—The original RCA cleaning process was based on a simple immersion technique. Several different and improved techniques have been introduced over the years, as will be discussed. The immersion procedure is done in vessels of fused silica to prevent leaching of aluminum, boron, and alkalis if Pyrex glass is used. A batch of wafers is immersed in the SC-1 or SC-2 solution under the prescribed conditions. The reaction is terminated by overflow quenching with cold DI water before the wafers are transferred to a flow rinse system with ultrafiltered DI water, followed by spin drying in a wafer centrifuge. Several types of refined wet bench immersion systems for automated processing are now available for large-scale production (17–19).

Centrifugal spray cleaning.—In 1978, FSI Corporation introduced the first centrifugal spray cleaning machine specifically designed for automatic operation with corrosive chemicals. The wafers rotate past a stationary spray column. Filtered acids and reagent solutions, including hot SC-1, SC-2, and DI water, are pressure-fed into a mixing manifold and then directed as a dispersed spray onto the spinning wafers. The spin-rinsed wafers are dried by high-speed spinning in heated nitrogen. A reduced volume of freshly mixed reagents is used and the process is faster than by immersion. The chemical cleaning efficiency, according to FSI, is comparable with that of immersion, but particles are removed more efficiently. Improved versions of this system (20) and other types of spray processing machines (17–19) are widely used but tend to require considerable maintenance.

Megasonic cleaning.—The original objective of the RCA cleaning process was the removal of contaminant films rather than particles. To complement this technique, the megasonic particle removal system was developed at RCA and first described in 1978 (21). A highly effective noncontact scrubbing action on both front and back side surfaces of the wafers is achieved by ultrahigh-frequency sonic energy while the wafers are submerged in the cleaning solution. The sonic waves of 550–800 kHz are generated by an array of piezoelectric transducers. Particles ranging in size from several micrometers down to about 0.3 μm can be efficiently removed with input power densities of 2–5 W/cm^2 . For comparison, ultrasonic systems operate typically at 20–80 kHz and require power densities of 1 p to 50 times that of the megasonic system but are much less effective for removing very small particles. Megasonic cleaning made it possible to remove simultaneously contaminant films and particles in one operation by combining the peroxide treatments with megasonics. The system allows removal of particles, organic contaminant films, and lightly adsorbed contaminants with diluted SC-1 solution at the ambient bath temperature of only 35°–45°C. Chemisorbed inorganics generally require higher temperatures (about 70°C) for complete desorption with SC-1 and SC-2, but no quantitative data are available as yet. A detailed paper on megasonic wafer cleaning was published in 1985 (22). Improved megasonic systems built under license from RCA have become available in the past few years from Verteq, Semiconductor Technology, and Ettek.

Closed system chemical cleaning.—A system termed "Full-Flow", developed in 1988 by CFM Technologies, Incorporated, is based on keeping the wafers stationary and enclosed in the system during the entire cleaning, rinsing, and drying process (23). The vessel containing the wafers is hydraulically controlled to remain filled with hot or cold process fluids, including SC-1 and SC-2, that flow sequentially and continuously over stationary wafers loaded in

cassettes. The repeated crossing through the gas/liquid phase boundaries in the immersion techniques is thereby eliminated. The system thus avoids recontamination problems encountered when wafers are pulled out from a liquid.

Chronological Literature Survey

Beginning in 1972, independent investigators examined and verified by various analytical methods the effectiveness of the RCA cleaning method published in 1970 (1). This section chronologically reviews references on silicon wafer cleaning pertaining specifically to hydrogen peroxide solutions, up to mid-1989.

In 1972 Henderson published results on the evaluation of SC-1/SC-2 cleaning, using high-energy electron diffraction and Auger electron spectroscopy as analytical methods (24). He concluded that the process is well suited for wafer cleaning prior to high-temperature treatments, as long as quartz ware is used for processing, as specified by us (1). An additional final step in HF solution after SC-1/SC-2 caused carbon contamination and surface roughening during vacuum heating at 1100°C due to loss of the protective 1.3 nm thick C-free oxide film remaining after SC-2. Maak et al. (1973) investigated the removal of inorganic contaminants, including Cu and heavy metals, from silica-coat polished wafers by several reagent solutions (25). Using Rutherford backscattering, they concluded that SC-1/SC-2 preoxidation cleaning removes all elements heavier than Cl. Sulfur and chlorine remained after either SC-1, SC-2, or other cleaning procedures at 10¹⁴/cm². SC-1/SC-2 cleaning eliminated Ca and Cu much more reliably than did HF-HNO₃. Amick (1978) reported the presence of Cl on Si after SC-2 and S after H₂SO₄-H₂O₂; he used spark source mass spectrometric analysis (26). In 1978 Kern and Deckert published a brief review of surface contamination and semiconductor cleaning as part of a book chapter on etching (3). Murarka et al. (1977) studied methods for oxidizing Si without generating stacking faults and concluded that SC-1/SC-2 prior to oxidation is essential for this purpose (27). Gluck (1978) discussed removal of gold from Si by a variety of solutions. The desorption efficiency of SC-1 was more effective than that for SC-2, but the recommended sequential treatment of SC-1 followed by SC-2 was found to be the most effective method at high gold surface concentrations (10¹⁴/cm² range) (28). Peters and Deckert (1979) investigated photoresist stripping by solvents, chemical agents, and plasma ashing. The SC-1 procedure was the only acceptable technique by which the residues could be removed completely (29). Burkman (1981) reported on desorption of gold with several reagent solutions by centrifugal spraying. SC-1 type solution was much more effective than H₂SO₄-H₂O₂, while a SC-2 type alone showed poor efficiency (30).

Phillips et al. (1983) applied SIMS (secondary ion mass spectroscopy) to determine the relative quantities of contaminants on Si. Cleaned wafers were purposely contaminated with gross quantities of numerous inorganic materials and then cleaned by immersion or spray techniques with various aggressive reagents including aqueous hot fuming HNO₃, and H₂SO₄-H₂O₂. The lowest residual concentrations for most impurity elements were obtained by spray cleaning with H₂SO₄-H₂O₂, followed by the SC-1/SC-2 type cleaning sequence (30). Goodman et al. (1983) demonstrated by minority-carrier diffusion-length measurements the effectiveness of SC-1/SC-2 for removing trace metals on Si (31). The author (1983) published a review of the subject on the occasion of the Citation Classic declaration of the original 1970-paper (32). In 1983 Watanabe et al. (33) reported dissolution rates of SiO₂ and Si₃N₄ films in SC-1. The rate of thermally grown SiO₂ in SC-1 during 20 min at 80°C was a constant 0.4 nm/min, a significant rate for structures with thin oxide layers. The etch rate of CVD Si₃N₄ was 0.2 nm/min under the same conditions. Measurements by the author in 1981 (and published in 1984), however, indicated much lower oxide dissolution rates under nearly identical conditions (34). Film thicknesses were measured by ellipsometry after each of four consecutive treatments in fresh 5:1:1 SC-1 at 85°C and totaled only 7.0 nm/60 min, or 0.09 nm/min. Under the same

conditions, 6:1:1 SC-2 showed no loss. Similar results averaging 0.13 nm/min were obtained with thermal SiO₂ films grown on lightly or heavily doped Si. Wafers from the same sets were used to determine the etch rates of exposed Si in SC-1 solutions with decreasingly lower H₂O₂ content. No etching or attack of Si occurred until the H₂O₂ was reduced by more than 75% (34).

Bansal (1984, 1985) reported extensive results in particle removal by spray cleaning from Si wafers with SC-1/SC-2, H₂SO₄-H₂O₂, and HF solution of various purity grades. He found the RCA cleaning solutions to be the most effective (35, 36). Schwartzman et al. (1985) described simultaneous removal of particles and contaminant films by megasonic cleaning with SC-1 solutions (22). Ichizaka and Shiraki (1986) showed that atomically clean Si surfaces for MBE can be prepared below 800°C in UHV by thermal desorption of a thin (0.5-0.8 nm), passivating oxide layer that protects from C contamination (37). It is formed in a series of wet oxidation (HNO₃, SC-1) and HF-stripping steps, terminating with an SC-2 type treatment. Wong and Kasper (1986) used XPS analysis to examine Si after wet chemical treatments. RCA cleaning without buffered HF stripping resulted in about 30% of the Si atoms in the top 1.0 nm being oxidized, whereas with a final RHF step less than one monolayer of suboxide coverage resulted (38). Grundner and Jacob (1986) conducted extensive studies of Si surfaces after treatment with SC-1/SC-2 or 5% HF solutions, using x-ray photoelectron and high-resolution electron energy loss spectroscopy. Oxidizing solutions produced hydrophilic surfaces, whereas HF solution led to hydrophobic surfaces consisting mainly of Si-H with some Si-CH₃ and Si-F (39). In 1988 Becker et al. (40) reported on decontamination by different reagent sequences. SIMS analysis was used to test for the removal of Na, K, Ca, Mg, Cr, Cu, Al, and particle impurities. The best cleaning sequence for metallics was H₂SO₄-H₂O₂/SC-1/HF/SC-2. Reversing the order of SC-1 and HF was most effective for particle removal and slightly less so for metal ions. Kawada et al. (1988) found by SIMS that Al on Si wafers originated from impure H₂O₂ used in SC-2. Very high concentrations resulted if Pyrex vessels were used in the processing instead of fused quartz (41). In 1986 McGillivray et al. (42) investigated effects of reagent contaminants on MOS capacitors. Low field breakdown was more prevalent if preoxidation cleaning with SC-2 was terminated with HF solution instead of omitting it. No other significant differences in electrical properties resulted from these two treatments.

Lampert (1987) examined growth and properties of oxide films on Si in various aqueous solutions, including SC-1 and SC-2 (43). Gould and Brane (1987) studied the influence of preoxidation cleaning on Si oxidation kinetics (44). They found significant rate variations depending on treatment (SC-1/SC-2/HF, SC-1, SC-2, HF, no clean). Ruyville (1987) reported on similar experiments and found that various preoxidation cleans seem to affect structure and/or composition of the subsequently grown oxide rather than the reactivity of the Si surface (45). Shuster and MacDowell (1987) found that sub-ppm levels of Al in H₂O₂ used for SC-1/SC-2 causes a substantial shift (up to 0.2V) in the saturation voltage of a dual dielectric. Aluminum concentrations on the water surface, and basic media such as SC-1, lead to 5 times higher levels than acid (SC-2) solutions (46). In 1987 Hara and Sabeoka reviewed wafer cleaning in a new chapter on wet etching (11). Probst et al. (1988) stated that for achieving predictable diffusion from implanted doped poly-Si into single-crystal Si, an SC-1/SC-2 treatment of the substrate prior to poly-Si deposition is imperative (46). Khilnani (1988) discussed various aspects of semiconductor cleaning, including the RCA process (12). Peterson (1988) showed that the sequencing of cleaning solutions (H₂SO₄-H₂O₂, SC-1, SC-2, HF) can have dramatic effects on particles levels (47). In 1989 Morota et al. (48) reported on the contamination of SC-1/SC-2 cleaned wafers by Na, K, Al, Cr, Fe, Ni, and Cu from solutions, showing that the absence or presence of an SiO₂ layer on the Si surface strongly affects adsorption. Desorption of Al and Fe was most effective with HF-H₂O, and that

of Cu and Cr with SC-1. Some authors (49) postulated that metals of high enthalpy of oxide formation adsorb on the oxidized Si surface by oxide formation, whereas metals of low ionization tendency deposit electrochemically on the bare Si. Gould and Irene (1989) studied the etching of native SiO_2 and Si in $\text{NH}_4\text{OH}-\text{H}_2\text{O}$, BHF, and SC-1 by ellipsometry. Severe Si surface roughness resulted from NH_4OH loss with BHF, and none with SC-1 (50). Ohmi et al. (1989) compared particle removal efficiency of several cleaning solutions. They found that 5:1:1 SC-1 efficiently removes particles larger than $0.5 \mu\text{m}$, but increases those smaller than $0.5 \mu\text{m}$ ("buds") unless the NH_4OH ratio was decreased to one half or less, in which case both types of particles were reduced efficiently. However, no processing conditions and effects of low- NH_4OH SC-1 on removal of chemical contaminant films were mentioned (51). Menon et al. (1989) evaluated effects of solution chemistry (5:1:1, SC-1, DI water) and particle composition on megasonic cleaning efficiency at various power levels. They concluded that cleaning efficiency depends on several factors and that megasonics can provide water cleanliness levels not previously attainable (52).

Alternative Cleaning Techniques

General.—Many techniques for cleaning silicon wafers have been tried over the years with various degrees of success. Some techniques are useful only for specific applications or may introduce undesirable side effects. For example, glow discharge techniques (53) such as plasma etching, effectively strip photoresist films but leave inorganic contaminants and metals behind. Various types of sputter-etching (53) can cause surface damage. Some techniques remain restricted to certain applications, such as plasma treatments for preparing small-geometry devices for metallization (54), or wet-chemical etching of the silicon to remove entire surface layers by etch dissolution (5, 11). The following few techniques have been found viable and, in some cases, can be a desirable addition or alternative to the processes based on hydrogen peroxide solutions.

Brush scrubbing, fluid jet, and ultrasonic techniques.—The removal of large particles (e.g., after sawing and lapping operations) has been accomplished since the early days with water scrubbing machines that dislodge particles hydrodynamically with brushes made of a hydrophilic material (such as nylon) while DI water or isopropyl alcohol is applied to the surface (55). A thin layer of fluid must be retained between the brush and the wafers by careful mechanical adjustment to prevent surface scratching (55). While many contradictory claims have been made (56), if properly maintained, brush scrubbing can be very effective for removing particles larger than $1 \mu\text{m}$ from planar and preferably hydrophilic wafer surfaces.

High-pressure fluid jet cleaning consists of a high-velocity jet of liquid sweeping over the surface at pressures of up to 4000 psi (55, 56). The liquid can be DI water or organic solvents. The shear forces effectively dislodge submicron particles and penetrate into dense topography, but damage to the water can result with improperly adjusted pressure (18).

Ultrasonic techniques use sonic energy of 30 kHz and above to dislodge particles. High-intensity sound waves generate pressure fluctuations that result in cavitation bubbles which upon collapsing, release enough energy to dislodge and disperse particles but can also lead to wafer damage (55). Menon et al. have recently investigated various cleaning liquids for removing particles from wafers by ultrasonic and spray jet techniques (57). DI water was best for removing polymeric particles, while ethanol-acetone (1:1) was best (better than Freon) for inorganic particles. Cleaning efficiency decreased with decreasing particle size. A unique acoustical cleaning system utilizing 30 kHz frequency and only DI water as medium was introduced by Estek in 1986 (18) but has been abandoned.

Choline cleaning.—In contrast to the mechanical techniques for particle removal discussed in the previous section, choline cleaning is a chemical treatment that removes

particles and some contaminant films but at the same time appears to add certain contaminants to the surface. Choline, which is trimethyl-2-hydroxyethyl ammonium hydroxide, was first proposed by Asano et al. in 1978 (58) as a replacement for inorganic bases for etching and cleaning. It is a strong and corrosive base without all elements and etches silicon like other bases. A formulation of the chemical is available from Mallinckrodt under the tradename "Summa-Clean SC-15 M," which is a dilute choline solution containing a surfactant and methanol. Etching of Si can be prevented by adding H_2O_2 as an oxidant (59). There is very little published information on this subject, most data being contained in proprietary technical reports with contradictory results. Poly- γ -ow engineering manufactures an automatic dual-chamber spray machine that uses a warm choline- H_2O_2 - H_2O mixture and a DI water spray rinse (18). In some procedures the mixture replaces only SC-1 in the RCA cleaning procedure. In 1989 Kaos discussed oxide defect densities as a function of various preoxidation cleans including choline- H_2O_2 - H_2O , HF- H_2O , RCA clean, and UV-ozone (50).

UV-ozone and other dry-cleaning techniques.—Irradiating a surface with short-wavelength UV from a mercury quartz lamp in the presence of oxygen is a powerful technique for removing many contaminants. Oxygen absorbs 185 nm radiation forming very active ozone and atomic oxygen (61). The technique is most suitable for oxidative removal of adsorbed organics, but is generally not effective for most inorganics or metals. Therefore, its use in the past has been limited, in general, to special applications, such as GaAs wafer cleaning. Improvements in oxide qualities have been attained by applying the technique after SC-1/SC-2/HF- H_2O , immediately before oxidation (62). Ruzyllo et al. (1989) have shown that UV- O_2 cleaning can replace SC-1 for removing organics (63), and Kaos reported improvements in properties of thermal oxide films (60).

Hornig (1988) investigated the use of dry ice snow for removing particles from wafers (64). Clean, liquid CO_2 from a tank is allowed to expand to form dry ice snow, which is blown across the surface. The sliding snow is quite effective for mechanically removing particles. Particle detachment by electrostatic techniques has been investigated but found to be impractical (12). In 1987 FSI Corporation introduced a processing system for anhydrous F_2 gas phase etching of oxide and silicate films at room temperature (65). Applications to device processing were published in 1988 (66, 67). The contamination problems inherent with HF- H_2O solutions were avoided and in combination with the UV-ozone technique constitutes part of an ultrapure, integrated dry cleaning process that can be carried out entirely in the gas phase and may replace conventional wet techniques. Removal of metallic impurities could be accomplished by use of a remote microwave plasma (68), by chlorine radical techniques (57) or by photo-induced desorption in reactant gases (69). These new processes being developed are all designed to remove contaminants at low temperatures as volatile compounds without damaging the surface.

Wafer Rinsing and Drying

The last steps in wafer cleaning are rinsing and drying; both are extremely critical because clean wafers become recontaminated very easily if not processed properly. Rinsing after wet cleaning is done with flowing high-purity and ultrafiltered high-resistivity DI water, usually at room temperature (34). Megasonic rinsing is advantageous (32). Centrifugal spray rinsing (20) and rinsing in a closed system (23) have the advantage that the wafers are not removed between cleaning, rinsing, and drying. Wafer drying after rinsing must be done by physical removal of the water rather than by allowing it to evaporate. Spin drying accomplishes this and has been the most widely used technique. Hot forced-air drying is a preferred technique with less chance for particle recontamination (21, 32). Capillary drying is based on capillary action and surface tension to remove the water. Individual wafers are pulled out of DI water at 80–85°C; less than 1% of the water remains and evaporates, leaving a particle-free surface (71). In solvent

vapor drying wet wafers are moved into the hot vapor of a high-purity solvent, usually IPA (isopropyl alcohol), which displaces the water. The wafers dry quickly and are particle-free when the cassette is withdrawn above the hot vapor zone. Commercial drying systems for IPA and for nonflammable solvent mixtures are available (23, 70). The purity of the solvent is extremely important, and the water content during processing must be closely controlled, preferably by continuous recycling (51, 70).

Conclusion

Processes and techniques for cleaning, rinsing, and drying bare and oxide-coated silicon wafers have been reviewed from the 1950s to the present. Wet chemical cleaning based on hydrogen peroxide solutions and implemented by several techniques is still the main process used in industry. However, new wafer surface preparation technologies based on dry processing in the gas or vapor phase are being developed that promise superior results.

A great deal of research activity is taking place in this important area of technology, as evidenced by the scheduled presentation of over 60 papers (not referenced herein) at the First International Symposium on Wafer Cleaning Technology in Semiconductor Device Manufacturing, October 18-19, 1989, at the Electrochemical Society Fall Meeting.

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Growth and Properties of LPCVD Titanium Nitride as a Diffusion Barrier for Silicon Device Technology

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ABSTRACT

Chemical vapor deposition has been used to deposit titanium nitride (TiN) on silicon wafers at low pressures in a cold-wall single-wafer reactor. Experiments are reported for pressures in the range of 100-300 mtorr and temperatures between 660°-700°C, with titanium tetrachloride and ammonia as reactants. Both hydrogen and nitrogen are evaluated as diluents. Deposition rates as high as 1000 Å/min have been achieved. The chemical nature of the films are evaluated by Auger and RBS techniques, while the morphology is depicted by SEM. For the most part, the films are stoichiometric and contain small quantities of oxygen, chlorine, and hydrogen. Film resistivities as low as 50 $\mu\Omega\text{-cm}$ are reported. Behavior of the TiN film as a diffusion barrier between silicon (boron doped) and aluminum, at annealing temperatures up to 650°C, is evaluated by measurements of contact resistance and diode leakage.

Coating of various metals with titanium nitride has been possible since the discovery in the 1920s of a chemical vapor deposition technique using electrically heated wires exposed to $\text{TiCl}_4 + \text{N}_2 + \text{H}_2$ gas mixtures (1, 2). In spite of the high temperatures required ($>1000^\circ\text{C}$), commercial applications for jewelry coating (3) (gold color) and tool coating (4) (wear resistance) have seen considerable success. With the advent of reactive physical vapor deposition techniques (5-8), where a discharge in nitrogen is created with titanium atoms either evaporated or sputtered from one electrode, low temperature depositions ($<500^\circ\text{C}$) became possible and applications of TiN coatings have become even more widespread. Other applications have been as a transparent heat mirror for architectural windows (9, 10), and as a high temperature diffusion barrier for silicon solar cells (11, 12).

Of particular interest in the present paper, is the application of thin TiN films to silicon device technology. Because of the concerns about exposure of circuits to high temperature processes, barrier films deposited by physical vapor techniques such as low temperature reactive sputtering (13-22) have been employed. However, as integrated circuit feature sizes shrink to submicron dimensions, the ability of physical techniques to uniformly coat high aspect ratio vias has become a concern. Accordingly, there has been an interest in developing a low temperature CVD process for deposition of thin films of TiN. One approach has been to explore plasma-enhanced CVD (PECVD) using TiCl_4 plus either nitrogen (23-25) or ammonia (27, 28). Another has been to investigate the low temperature thermal CVD process possible using TiCl_4 + NH_3 , where depositions are possible at temperatures as low as 450°C. One recent investigation has focused on a low pressure CVD process (LPCVD) where many wafers are coated at one time in a hot wall tube reactor (29). Two others describe a LPCVD process in a cold-wall single-wafer reactor (30, 31). In this paper we elaborate on the latter approach.

Experimental

The titanium nitride depositions were carried out in a single-water cold-wall experimental reactor shown schematically in Fig. 1 (30). The chamber was stainless steel and enclosed a water and air-cooled lamp assembly used to heat the water. A single 10 kW tungsten halogen lamp

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was employed that can heat a 4 in. wafer to 700°C rapidly. A load lock was used to maintain an oxy gen and water vapor-free deposition environment.

Reactive gases were introduced through a showerhead gas distributor several inches above the wafer. The TiCl₄ and NH₃ were introduced through two separate lines and mixed for the first time in the shower head. As long as these two gases are mixed close to the hot wafer on which the deposit is to be made, the formation of NH₄Cl can be avoided as has been demonstrated in another experiment similar to this one (31).

Before beginning $TiCl_4$ or NH_3 flows, a nitrogen flow was established in the $TiCl_4$ line downstream of the $TiCl_4$ bottle. Next the $TiCl_4$ flow was initiated and after it was established then the NH_3 flow was introduced. This procedure kept $TiCl_4$ and NH_3 from mixing in the $TiCl_4$ line and causing solid deposits there.

All of the gases were introduced through mass flow controllers (MFCs), including the TiCl_4 vapor which was obtained by heating TiCl_4 liquid to 40°C . The TiCl_4 line was heated to 50°C to prevent any condensation of this vapor. Since the pressure of the TiCl_4 vapor at 40°C was only 5 torr, we calibrated our Unit MFC (UFC-100) by measuring the time it took for a specified nitrogen mass flow (supplied at 40 torr) to increase the pressure in our chamber from 100 to 200 mtorr. We then repeated this measurement when the nitrogen was supplied at 10 psi. By this method,

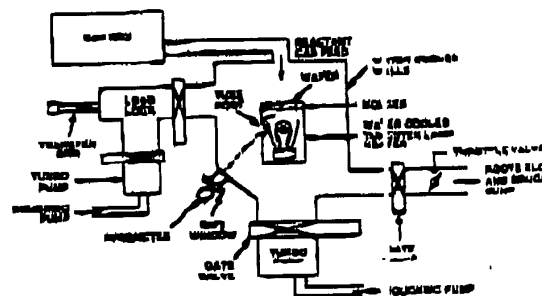


Fig. 1. Schematic of CVD reactor / system